

Origin of the anomaly in diffuse scattering from disordered Pt-V alloys

Igor Tsatskis*

Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, United Kingdom

An explanation of the anomalous concentration dependence of diffuse scattering from the Pt-V alloy system (splitting of the (100) short-range order intensity peak with increasing Pt content) is proposed. The effect is attributed to the competition between the interaction and self-energy curvatures. A similar temperature behaviour is predicted.

PACS: 05.50+q, 61.66.Dk, 64.60.Cn

In this Letter we put forth an explanation of recently published [1] unusual experimental and Monte Carlo (MC) results for diffuse scattering from disordered Pt-V alloys. The short range order (SRO) diffuse intensity (hereafter referred to simply as the intensity) for two alloys, Pt₃V at 1393 K and Pt₈V at 1224 K, was obtained in Ref. [1] from in situ neutron scattering data by separating different contributions to the total intensity, and a qualitative difference between the two intensity distributions was found. The Pt₃V intensity showed a simple peak at the (100) position, while in the case of the Pt₈V alloy this peak was split along the (*h*00) line. The Pt₈V intensity thus exhibited a saddle point, rather than a maximum, at the (100) position. On the other hand, the inverse Monte Carlo (IMC) interactions determined from the SRO results were nearly the same for both alloys (pairwise interactions were assumed), indicating that the whole effect might be of statistical-mechanical origin. To verify this conjecture, the set of the IMC interactions found for the Pt₃V alloy was used to generate the MC intensity for the Pt₈V composition at 410 K (50 K above the calculated MC transition temperature), and the splitting of the (100) peak was indeed observed. At the same time, the MC intensity for the Pt₃V alloy was in good agreement with its experimental counterpart, showing no splitting. The conclusion is, therefore, that the same interaction can lead to intensity peaks at different positions, depending on concentration (and, in fact, on temperature, since the measurements and MC simulations for the two alloys were carried out at different temperatures). This conclusion is in clear contradiction with the standard mean-field arguments, according to which peaks of the intensity should always correspond to minima of the pair interaction in the reciprocal space.

Thus, the question arises about the origin of the observed anomaly. It is shown below that such behaviour is the result of the competition between the reciprocal-space curvatures of the interaction and self-energy terms entering the formula for the intensity on an equal footing. The splitting develops when the self-energy curvature exceeds the curvature of the interaction term. In the mean-field approach the wavevector dependence of the self-energy is ignored, hence the inability to account for effects similar to observed in Ref. [1]. Indeed, the formally exact expression for the SRO diffuse intensity

is [2]

$$I(\mathbf{k}) = \frac{1}{c(1-c)[- \Sigma(\mathbf{k}) + 2\beta V(\mathbf{k})]} . \quad (1)$$

Here \mathbf{k} is the wavevector, $I(\mathbf{k})$ the intensity in Laue units, c the concentration, $\beta = 1/T$, T the temperature in energy units, $V(\mathbf{k})$ the Fourier transform of the pair ordering potential V_{ij} ,

$$V_{ij} = \frac{1}{2}(V_{ij}^{AA} + V_{ij}^{BB}) - V_{ij}^{AB} , \quad (2)$$

and the potential $V_{ij}^{\alpha\beta}$ corresponds to the interaction between an atom of type α at site i and an atom of type β at site j . Finally, $\Sigma(\mathbf{k})$ is the self-energy of the pair correlation function (PCF); the PCF in the \mathbf{k} -space representation is proportional to $I(\mathbf{k})$. Apart from the wavevector, Σ also depends on the concentration and the temperature. Eq. (1) is one of the possible forms of the Dyson equation [3] which is satisfied by the PCF; this issue is discussed in considerable detail elsewhere [4]. In the mean-field Krivoglaz-Clapp-Moss (KCM) approximation [5],

$$I^{KCM}(\mathbf{k}) = \frac{1}{1 + 2c(1-c)\beta V(\mathbf{k})} , \quad (3)$$

however, Σ is a function of concentration only,

$$\Sigma^{KCM} = -\frac{1}{c(1-c)} . \quad (4)$$

Another, much better approximation for $I(\mathbf{k})$ is the spherical model (SM) [6] (also known as the Onsager cavity field theory [7]),

$$I^{SM}(\mathbf{k}) = \frac{1}{c(1-c)[- \Sigma^{SM} + 2\beta V(\mathbf{k})]} , \quad (5)$$

where Σ^{SM} is a number determined from the sum rule

$$\alpha_{000} = \frac{1}{\Omega} \int d\mathbf{k} I(\mathbf{k}) = 1 . \quad (6)$$

Here α_{lmn} is the SRO parameter for the coordination shell lmn , $I(\mathbf{k})$ is the Fourier transform of α_{lmn} , and the integration is carried out over the Brillouin zone of volume Ω . As follows from Eqs. (5) and (6), the SM

TABLE I. Nine IMC pair interactions V_{lmn} for the Pt₃V alloy and first nine SRO parameters α_{lmn} for the Pt₃V and Pt₈V alloys obtained in Ref. [1] from the experimental diffuse intensities [8]. Note the factor of 2 difference between the definitions of V_{lmn} in Ref. [1] and the present work.

lmn	V_{lmn} , Pt ₃ V	α_{lmn} , Pt ₃ V	α_{lmn} , Pt ₈ V
110	89.0	-0.1619	-0.1234
200	-14.0	0.2144	0.1505
211	12.6	-0.0031	-0.0214
220	11.2	0.0700	0.0215
310	9.8	-0.0589	-0.0049
222	0.38	0.0141	0.0121
321	-1.76	-0.0065	-0.0020
400	4.6	0.0423	0.0136
330	-8.0	-0.0029	0.0314

also takes into account the temperature dependence of the self-energy. Nevertheless, in the SM the self-energy is still wavevector-independent.

Meanwhile, in our case the wavevector dependence of the self-energy is crucial. Let us consider the behaviour of all \mathbf{k} -dependent quantities in Eq. (1) as functions of the deviation k of the wavevector from the (100) position along the $(h00)$ line. We assume that $V(k)$, similarly to the case of the Pt₃V alloy, has a simple minimum at $k = 0$ (see Fig. 3b below). Mathematically, the presence or absence of the splitting of the (100) intensity peak is controlled by the sign of the second derivative $I'' = (\partial^2 I / \partial k^2)_{k=0}$. From Eq. (1) it follows that

$$I'' = c(1 - c)I^2(0) (\Sigma'' - 2\beta V'') . \quad (7)$$

Eq. (7) shows that the self-energy curvature Σ'' can dominate if the (100) minimum of $V(k)$ is shallow (V'' is small). In particular, it is Σ'' that controls the fine structure (single- vs. double-peak) of the $k = 0$ maximum of $I(k)$ in the limiting case of vanishing V'' . Thus, according to Eq. (7) the splitting occurs when $\Sigma(k)$ is a convex-down function and its (100) curvature is greater than that of the interaction term $2\beta V(k)$. In contrast to this, in the KCM and SM approximations the self-energy is \mathbf{k} -independent (i.e. flat), and the peak splitting occurs only when the interaction has a double minimum.

Our next step is to make some estimates using available experimental and IMC data. Listed in Table I are the IMC interaction parameters V_{lmn} for the Pt₃V alloy used in Ref. [1] in the direct MC simulations for both Pt₃V and Pt₈V compositions, and the SRO parameters α_{lmn} for the two alloys [8]. These data can be used to estimate the curvatures of the interaction and the self-energy terms in Eq. (1). For an arbitrary matrix f_{ij} defined on the FCC lattice, the second derivative f'' of its Fourier transform $f(\mathbf{k})$ is

$$f'' = 8\pi^2 (f_{110} - f_{200} - 2f_{211} - 4f_{220} + 10f_{310} - 4f_{222} + 12f_{321} - 4f_{400} + 9f_{330}) , \quad (8)$$

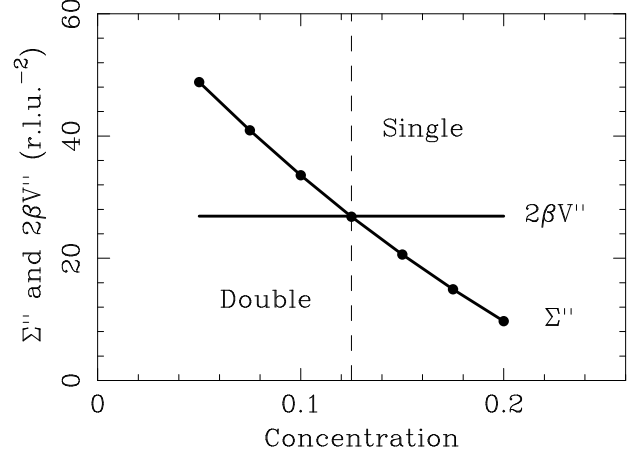


FIG. 1. Derivatives Σ'' and $2\beta V''$ (Eq. (7)) as functions of concentration at $T = 1224$ K. The type of the (100) intensity maximum (single or double peak) is indicated.

when, as in Table I, first nine coordination shells are taken into account; the factor π^2 reflects the fact that the wavevector is measured in reciprocal lattice units (r.l.u.). Using Eq. (8), the curvature V'' of the Pt₃V interaction can be easily calculated, and the result at 1393 K is $2\beta V'' = 23.6$ r.l.u.⁻². To calculate the curvature of the self-energy, we use the expansion of its off-diagonal (in the direct-space representation) part in powers of the SRO parameters (for short, the α -expansion, or AE), of which two first non-zero orders are available [2],

$$\Sigma_{lmn} = a\alpha_{lmn}^2 + b\alpha_{lmn}^3 + O(\alpha^4) , \quad lmn \neq 000 , \quad (9a)$$

$$a = \frac{(1 - 2c)^2}{2[c(1 - c)]^2} , \quad (9b)$$

$$b = \frac{[1 - 6c(1 - c)]^2 - 3(1 - 2c)^4}{6[c(1 - c)]^3} . \quad (9c)$$

Eqs. (9) were derived in the context of the γ -expansion method (GEM) [2,9]. Using Eqs. (8), (9) and α_{lmn} from Table I, we get $\Sigma''(\text{Pt}_3\text{V}) = 2.7$ r.l.u.⁻² and $\Sigma''(\text{Pt}_8\text{V}) = 58.5$ r.l.u.⁻². It is immediately seen that

$$\Sigma''(\text{Pt}_3\text{V}) < 2\beta V''(\text{Pt}_3\text{V}) < \Sigma''(\text{Pt}_8\text{V}) , \quad (10)$$

with a considerable difference between each two values. The fact that SRO for the two alloys was measured at different temperatures is not very important here; $2\beta V'' = 26.9$ r.l.u.⁻² at 1224 K. Eq. (10) suggests that the set $\{V_{lmn}\}$ from Table I leads to the splitting of the (100) intensity peak for the Pt₈V composition at 1224 K, whereas in the case of the Pt₃V alloy at 1393 K a simple peak should be observed (see Eq. (7)). Note, however, that these estimates are not fully consistent, since the interaction parameters for the two alloys are similar but not identical. Furthermore, in the approximate Eq. (9a) the experimental values of the SRO parameters

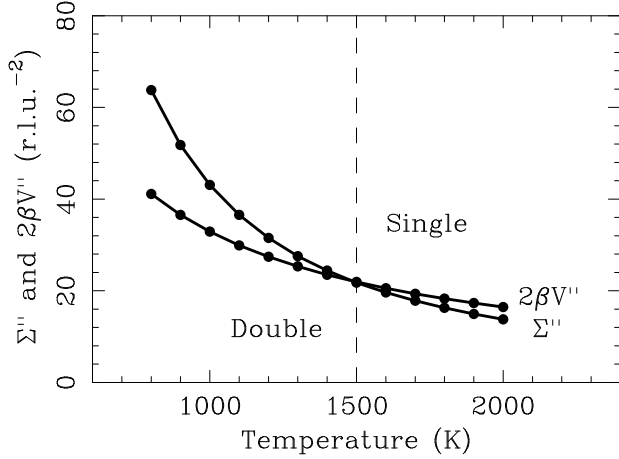


FIG. 2. The same derivatives as in Fig. 1 but as functions of temperature for $c = 1/9$.

were used, though they should have instead been calculated self-consistently. Nevertheless, Eq. (10) clearly shows the tendency for the self-energy curvature to become greater than the curvature of the interaction term when the concentration of Pt increases.

To confirm these preliminary considerations, we carry out the self-consistent AE calculations. The complete set of the AE equations constituted by Eqs. (1), (6) and (9) is solved for given interaction parameters, temperature and concentration to find the SRO parameters, self-energy and intensity. A particular AE approximation is defined by neglecting fourth- and higher-order terms and including only finite number of coordination shells in Eqs. (9) for Σ . The zero-order approximation of the AE approach ($\Sigma_{lmn} = 0, lmn \neq 000$) coincides with the SM [2]. Here all calculations are performed using the set of interactions V_{lmn} for the Pt_3V alloy (Table I) and nine-shell approximation for the self-energy; inclusion of additional shells leads to negligible corrections.

The results of the calculations are shown in Figs. 1-4. Fig. 1 presents behaviour of the curvatures Σ'' and $2\beta V''$ with concentration at 1224 K. The $\Sigma''(c)$ curve crosses the horizontal line $2\beta V'' = 26.9 \text{ r.l.u.}^{-2}$ (the derivative $2\beta V''$ is concentration-independent) at approximately $c = 1/8$; according to Eq. (7), at this point the second derivative I'' vanishes. At greater concentrations $\Sigma'' < 2\beta V''$, so that $I'' < 0$ and the intensity has a simple maximum at the (100) position. On the contrary, when the concentration is below this value, as in the case of the Pt_8V alloy, the curvature of the self-energy exceeds that of the interaction term, and the (100) intensity peak splits along the (h00) line. This is precisely what was found in Ref. [1].

Furthermore, very simple arguments show that the splitting of the (100) intensity peak can develop also when temperature decreases at fixed concentration. In-

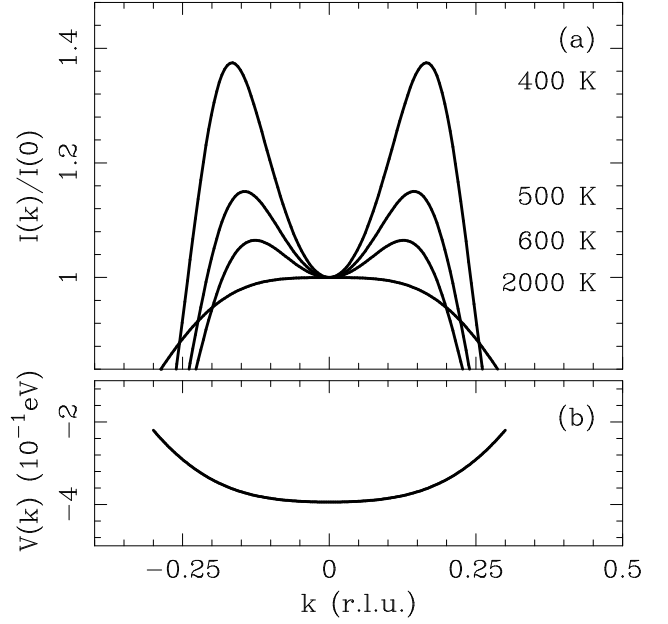


FIG. 3. (a) Normalized intensity $I(k)/I(0)$ for the Pt_8V composition at indicated temperatures and (b) the interaction $V(k)$ for the Pt_3V alloy.

deed, we have just seen that this peak splits for the Pt_8V composition at 1224 K if the interaction for the Pt_3V alloy which has a simple minimum at the (100) position is used. However, at high enough temperatures the asymptotically correct KCM formula (3) is valid, and the shape of the intensity follows that of $V(\mathbf{k})$. This means that the transition from single- to double-peak structure of the (100) intensity maximum occurs with decreasing temperature. This conclusion is illustrated in Fig. 2, where the same curvatures as in Fig. 1 are shown as functions of temperature for the Pt_8V composition. The compensation of the curvatures of the two terms in Eq. (1) occurs here at about $T = 1500 \text{ K}$. Profiles of the normalized intensity $I(k)/I(0)$ at different temperatures and of the interaction $V(k)$ are displayed in Fig. 3. The positions $\pm k_0$ of the intensity maxima and ratio $I(k_0)/I(0)$ at 400 K agree well with the MC values $k_0 = 0.2 \text{ r.l.u.}$ and $I(k_0)/I(0) = 1.3$ for 410 K estimated from Fig. 4 in Ref. [1]. Fig. 4 summarizes the findings of the present work, showing what can be called a “c-T phase diagram” for the (100) intensity peak. The line there is a set of points at which $I'' = 0$; crossing this line in any direction changes qualitatively the fine structure of the (100) maximum (single to double peak or vice versa).

It is necessary to note that the positions of the resulting $I(\mathbf{k})$ peaks depend on the temperature and the concentration, as follows, e.g., from Fig. 3a. Here it is possible to draw a formal analogy with the Landau theory of second-order phase transitions [10]. Let us consider the change of the intensity with temperature and

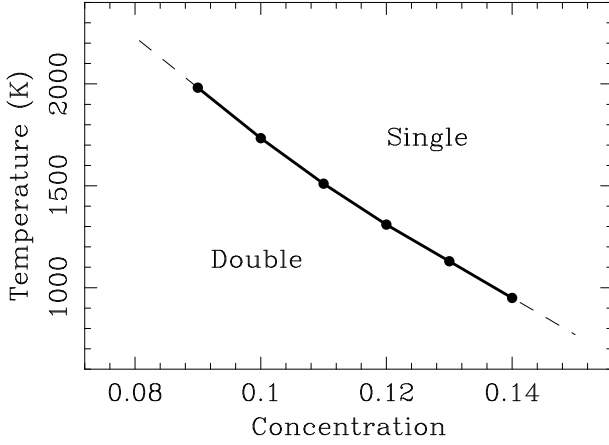


FIG. 4. “c-T phase diagram” for the (100) intensity peak.

assume that I'' vanishes at some temperature T_0 . Then, for temperatures close to T_0 and wavevectors near the (100) position, we have

$$I^{-1}(k) = I^{-1}(0) + \frac{1}{2}Ak^2 + \frac{1}{4}Bk^4, \quad (11)$$

where $A = c(1-c)[- \Sigma'' + 2\beta V''] = \tilde{A}(T - T_0)$, \tilde{A} and B are positive constants, and only the lowest-order terms are retained in the expansions of A and B in powers of $T - T_0$. The same expansion can be written using concentration instead of temperature. The inverse intensity thus has exactly the form of the Landau free energy functional, with k playing the role of the order parameter. Therefore, at small negative $T - T_0$ values the splitting increases as $(T_0 - T)^{1/2}$. Contrary to the corresponding result of the genuine Landau theory, the obtained bifurcation exponent is exact, since the intensity is an analytical function of the wavevector and can legitimately be expanded into the Taylor series. The temperature (concentration) dependence of the peak positions is shown schematically in Fig. 5.

In conclusion, we have put forward an explanation of the experimental and MC observations concerning the unusual concentration dependence of SRO diffuse scattering from the Pt-V alloy system. It was found in Ref. [1] that the same set of interaction parameters could produce qualitatively different intensity distributions at different concentrations, in this case simple and split (100) intensity peaks for the Pt_3V and Pt_8V compositions, respectively. In this Letter the observed anomaly is attributed to the competition between the reciprocal-space curvatures of the two terms in the expression for the SRO diffuse intensity. Currently used analytical theories of SRO neglect one of the curvatures, that of the self-energy (i.e. the \mathbf{k} -dependence of the latter); it has been shown how to overcome this difficulty by using the AE approach. The proposed theory predicts an analogous temperature dependence of the intensity and varying positions of the

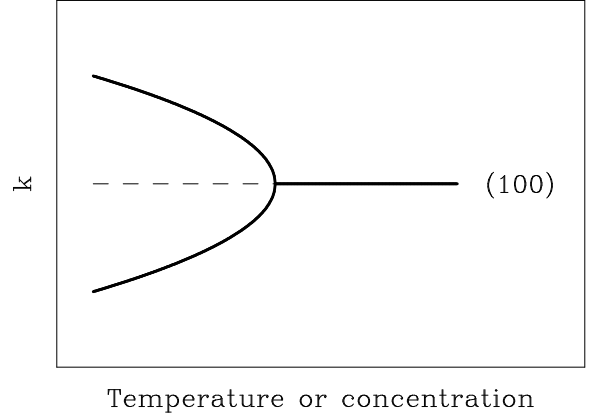


FIG. 5. Schematic temperature (concentration) dependence of the intensity peak positions.

resulting intensity spots in the split-peak regime.

The author thanks D. Le Bolloc’h for communicating results of Ref. [1] prior to publication and useful correspondence.

* E-mail: it10001@cus.cam.ac.uk. Former name: I. V. Masanskii

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